

NO DRAWINGS.

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COMPLETE SPECIFICATION.

Improvements in or relating to the Oxychlorination of Olefines.

We, THE DISTILLERS COMPANY LIMITED, a British Company, of 12 Torphichen Street, Edinburgh 3, Scotland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the oxychlorination of olefines and in particular to the oxychlorination of ethylene and is an improvement in or modification of that described in our co-pending Application No. 14836/61 (cognate) (Serial No. 932,130).

Application No. 14836/61 (cognate) (Serial No. 932,130) describes and claims a process for the production of chlorinated hydrocarbons which comprises contacting a feed containing an olefin, hydrogen chloride and molecular oxygen in the vapour phase at elevated temperature with a catalyst comprising copper deposited on alumina, prepared by heating activated alumina, prior to deposition of the copper, to a temperature of from 800° to 1400° C. In accordance with particular embodiments of this invention the catalyst may also contain an alkali metal salt and a salt or salts of iron or the rare earth metals, i.e. metals of atomic Nos. 57 to 71 inclusive such as cerium, lanthanum and neodymium.

It has now been found that the alkali metal salts may be partially or completely replaced by alkaline earth metal salts or hydroxides and in particular magnesium salts or magnesium hydroxide.

Accordingly the present invention is a process for the production of chlorinated hydrocarbons comprising contacting a feed containing an olefine, hydrogen chloride and molecular oxygen in the vapour phase at

elevated temperature with a catalyst comprising copper deposited on activated alumina, the latter having been heated prior to deposition of the copper to a temperature of from 800° to 1400° C. as claimed in British Application No. 14836/61 (cognate) (Serial No. 932,130) characterised in that the catalyst contains an alkaline earth metal salt, or hydroxide.

By the term "alkaline earth metal" herein is meant metals of Group IIA of the Periodic Classification due to Deming. Examples of such metals include, calcium, barium, strontium and magnesium.

The proportions of alkaline earth metal salt or hydroxide which are employed are suitably such as to provide from 0.2 to 10% by weight of the catalyst and alumina support of alkaline earth metal ion.

The alkaline earth metal salt or hydroxide may be incorporated with the catalyst for example by impregnation of the alumina before or after heat treatment with a solution of alkaline earth metal salt. The impregnation may be carried out before, after or simultaneously with the deposition of copper. Suitable alkaline earth metal salts include chlorides and/or nitrates. Organic salts such as formates, oxalates and/or acetates may also be used. The catalyst may contain more than one alkaline earth metal salt or hydroxide. As indicated above the use of magnesium salts or magnesium hydroxide is particularly preferred.

The alumina employed as the support material is obtained by heating activated alumina for not less than 2 hours and preferably up to about 24 hours. Preferred heat treatment temperatures are in the range 800 to 1100° C.

The catalyst used in the process may com-

prise copper oxide or copper chloride which may be applied to the alumina support in any suitable manner. For example, the alumina, after heat treatment, may be impregnated directly with a solution of copper chloride, dried, and used as such in the reactor. Alternatively the alumina may be impregnated with a solution of a copper salt, e.g. the nitrate or formate which is then converted into copper oxide within the pores of the alumina by either thermal decomposition or chemical hydrolysis followed by drying. In those instances where the catalyst is copper oxide formed by the thermal decomposition of a copper salt impregnated in the alumina, it may only be necessary to dry the alumina after impregnation and allow the thermal decomposition to the oxide to take place during the oxychlorination reaction at the reaction temperatures employed. The catalyst/alumina support mixture should preferably contain about 0.5 to 5% by weight of copper.

The catalyst may also contain salts of iron or the rare earth metals the presence of which have been found to reduce the volatility of the copper content of the catalyst.

By the term "rare earth metal" is meant those metals of atomic Nos. 57 to 71 inclusive such as cerium, lanthanum or neodymium.

The proportions of the iron or rare earth metal salt employed are suitably such as to provide from 0.2 to 10% by weight of the catalyst, alumina support and alkaline earth metal salt or hydroxide, of iron or rare earth metal ion.

The iron or rare earth metal salt may be incorporated with the catalyst in any suitable manner, for example before, after or simultaneously with the incorporation of the alkaline earth metal salt or hydroxide by impregnation of the alumina before or after heat treatment with a solution of a suitable iron or rare earth metal salt. Suitable iron or rare earth metal salts include chlorides and nitrates. Organic salts such as formates, oxalates and acetates may also be used. The catalyst may contain more than one iron or rare earth metal salt.

In carrying out the process the supported catalyst may be employed in a fixed bed in the form of pellets or granules or in a fluidised or moving bed.

The olefin fed to the reaction may be for example ethylene or propylene, or mixtures of the these olefines. The preferred olefin is ethylene.

The relative proportions of reactants in the feed may correspond substantially with the stoichiometric requirements of the reaction being carried out. In operation however it may be desirable to employ either an excess of the olefin and/or oxygen to obtain maximum conversion to product. The oxy-

gen in the feed may be provided by any suitable molecular oxygen containing gas, e.g. air, although it will be appreciated that recovery and recycle of reactants is facilitated by use of pure undiluted molecular oxygen.

Reaction temperatures may suitably range from 225° to 500° C. The contact time may range from $\frac{1}{10}$ th to 30 seconds and is preferably about 5 to 15 seconds. The reaction may suitably be carried out under pressure e.g. from 1 to 7 atmospheres absolute.

The hydrogen chloride feed may be provided from waste hydrogen chloride from the hydrolysis of 1,2-dichloroethane to produce vinyl chloride. The hydrogen chloride may also be diluted or partially replaced by chlorine.

The results obtained by use of alkaline earth metal salts or hydroxides in place of alkali metal salts are illustrated in the following example.

EXAMPLE.

5.36 parts by weight of cupric chloride dihydrate, 4.6 parts by weight of magnesium chloride hexahydrate and 3.25 parts by weight of technical cerium chloride were dissolved in the minimum amount of water and used to impregnate 42 parts by weight of commercial activated alumina in the form of $\frac{1}{8}$ " diameter pellets which had previously been heated for 24 hours at 1060° C. The mixture was evaporated to dryness with constant stirring and after drying at 110° C., contained 4% copper, 4% cerium and 1.1% magnesium.

2,450 parts by volume/hour of ethylene, 4,655 parts by volume/hour of hydrogen chloride and 5,922 parts by volume/hour of air were mixed and passed over 36 parts by volume of the catalyst in a fixed bed isothermal reactor at 300° C. The percentage conversion of hydrogen chloride to chlorinated products was 94.7% and 1.3% of the ethylene formed carbon dioxide.

WHAT WE CLAIM IS:—

1. A process for the production of chlorinated hydrocarbons which comprises contacting a feed containing an olefine, hydrogen chloride and molecular oxygen in the vapour phase at elevated temperature with a catalyst comprising copper deposited on activated alumina, the latter having been heated prior to deposition of the copper to a temperature of from 800° to 1400° C. as claimed in British Application No. 14836/61 (cognate) (Serial No. 932,130) characterised in that the catalyst contains an alkaline earth metal salt or hydroxide.

2. A process as claimed in Claim 1 wherein the alkaline earth metal salt or hydroxide is a salt or hydroxide of magnesium.

3. A process as claimed in Claim 1 or 2 wherein the alumina support either before or after heat treatment is impregnated with a solution of the alkaline earth metal salt or hydroxide. 5
4. A process as claimed in Claim 3 wherein impregnation of the alumina with the alkaline earth metal salt or hydroxide solution is carried out before, after or simultaneously with the deposition of the copper catalyst. 10
5. A process as claimed in any of the preceding claims wherein the alkaline earth metal salt or hydroxide is the chloride, or nitrate, formate, oxalate or acetate of the alkaline earth metal. 15
6. A process as claimed in any of the preceding claims wherein the proportion of alkaline earth metal salt or hydroxide present is such as to provide from 0.2 to 10% by weight of the catalyst/alumina mixture of alkaline earth metal ion. 20
7. A process as claimed in any of the preceding claims wherein the alkaline earth metal salt or hydroxide promoted catalyst is employed in admixture with at least one salt of iron or a rare earth metal as hereinbefore defined. 25
8. A process as claimed in Claim 7 wherein the alumina support either before or after heat treatment is impregnated with a solution of the iron or rare earth metal salt. 30
9. A process as claimed in Claim 8 wherein impregnation of the alumina support with a solution of the iron or rare earth metal salt is carried out simultaneously with the impregnation with the alkaline earth metal salt solution. 35
10. A process as claimed in Claims 7 to 9 wherein the iron or rare earth metal salt is the chloride, nitrate, formate, oxalate or acetate. 40
11. A process as claimed in Claims 7 to 10 wherein the proportion of the iron or rare earth metal salt present is such as to provide from 0.2 to 10% by weight of the catalyst, alumina support and alkaline earth metal salt or hydroxide of the relevant metal ion. 45
12. A process as claimed in any of the preceding claims wherein the olefine is ethylene or propylene. 50
13. A process as claimed in any of the preceding claims wherein the hydrogen chloride employed is waste hydrogen chloride from the pyrolysis of 1,2-dichloroethane to produce vinyl chloride. 55
14. A process as claimed in any of the preceding claims wherein the hydrogen chloride is diluted or partially replaced by chlorine. 60
15. A process as claimed in any of the preceding claims carried out at temperatures in the range 225° to 500° C. 65
16. A process as claimed in any of the preceding claims carried out at a contact time of 0.1 to 30 seconds.
17. A process as claimed in any of the preceding claims carried out under an increased pressure in the range from 1 to 7 atmospheres absolute. 70
18. A process for the production of chlorinated hydrocarbons substantially as hereinbefore described with reference to the example. 75
19. Chlorinated products when obtained by a process as claimed in any of the preceding claims.

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